MINIREVIEW

Biomass-derived renewable aromatics: selective routes and outlook for *p*-xylene commercialisation

Andy Maneffa, [a] Peter Priecel, [a] Jose A. Lopez-Sanchez*[a]

Abstract: Methylbenzenes are among the most important organic chemicals today and, among them, *p*-xylene deserves particular attention because of its production volume and its application in the manufacture of polyethylene terephthalate (PET). There is great interest in producing this commodity chemical more sustainably from biomass sources, particularly driven by manufacturers willing to produce more sustainable synthetic fibres and PET bottles for beverages. A renewable source for *p*-xylene would allow to achieve this goal with minimal disruption to existing processes for PET production. Despite the fact that recently some routes to renewable *p*-xylene have been identified, there is no clear consensus on their feasibility or implications. We have critically reviewed the current state of the art with focus on catalytic routes and possible outlook for commercialisation. Pathways to obtain *p*-xylene from a biomass-derived route include methanol-to-aromatics (MTA), ethanol dehydration, ethylene dimerization, furan cycloaddition or catalytic fast pyrolysis and hydrotreating of lignin. Some of the processes identified suggest near-future possibilities but also more speculative or longer-term sources for synthesis of *p*-xylene are highlighted.

1 Introduction

More than 35 million metric tons of *para*-xylene (*p*-xylene, Figure 1) were produced in 2010 globally[1] with the vast majority of this being utilised in the production of terephthalic acid (TA, Figure 1).[2]

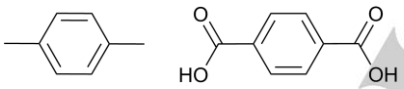
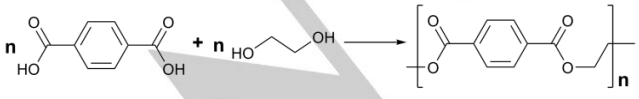


Figure 1. Structural formula of p-xylene (left) and TA (right).

In turn, TA is primarily converted into polyester-based materials, in particular to polyethylene terephthalate (PET) via the polycondensation of TA with ethylene glycol (Scheme 1).[3]



[a] Mr. A. Maneffa, Dr. P. Priecel, Dr. J.A. Lopez-Sanchez
Department of Chemistry
University of Liverpool
Crown Street, L69 7ZD Liverpool, United Kingdom
E-mail: jals@liverpool.ac.uk

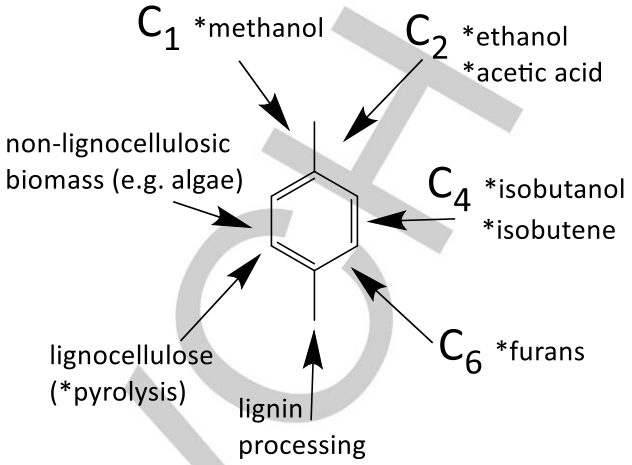
Scheme 1. Synthesis of PET via the polycondensation of TA and ethylene glycol.

Currently, most of the TA used in the manufacture of PET is derived via variation of oxidation of *p*-xylene[3-4] by Mid-Century/BP, Witten and Eastman processes[4b] making *p*-xylene both a valuable and very important commodity chemical. Industrially, *p*-xylene, along with various other aromatics, is typically obtained from refining of gasoline followed by a series of subsequent separation processes.[5] More recently, novel methods of *p*-xylene production have been explored,[6] although they are all ultimately reliant on the use of petroleum derived chemicals. Gradually diminishing oil and fossil fuel reserves, coupled with the negative environmental stigma that the use of such resources create, has generated interest in the development of renewable and more sustainable alternatives. There is great interest in producing this commodity chemical more sustainably, this is particularly driven by manufacturers willing to produce more sustainable synthetic fibres and PET bottles for beverages. A renewable source for *p*-xylene would allow to achieve this goal with minimal disruption to existing processes for PET production. On the other hand, biomass has been touted as being a promising source to both important high-volume low value and high value chemicals.[7] It is envisioned that eventually, such processing could take place within centralised facilities, termed 'biorefineries', where biomass will be converted into a myriad of different useful products including transportation fuels, energy and platform chemicals including *p*-xylene. In some aspects, a modern biorefinery can resemble the archetypical petroleum refinery which has evolved over the last 100 years and this is seen by many as a vital necessity as we go further into the 21st century.[8]

The production of biomass-derived *p*-xylene has received a large amount of recent interest from academic and industrial groups alike and several different biobased routes to *p*-xylene have been developed. Most of them are derived from the three abundant biopolymers: starch, cellulose and hemicellulose. Generally, at least one of these biopolymers is present in any source of terrestrial biomass. Many such sources are well known (e.g. the seeds of oryza sativa/glaberrima, commonly known as 'rice') and highly cultivated, typically for food. However, lignocellulose is a more sustainable feedstock for chemicals as it is non-edible and abundant across most areas of the world.[9] In addition to cellulose and hemicellulose, lignocellulosic biomass typically consists of *ca.* 20 % lignin,[10] a group of highly related macromolecules of difficult characterisation and composed of cyclic aromatics that are typically interconnected by ether linkages. Despite lignin's obvious attractiveness as an aromatic source, no selective, simple and effective process for the

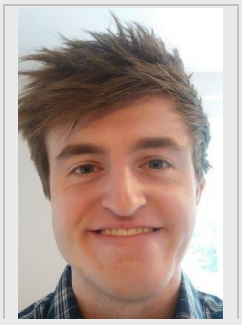
conversion of lignin to useful chemicals currently exists and this is an area that requires further research efforts.[11]

This paper reviews the state of the art in biomass-derived routes to *p*-xylene, with particular attention being paid to the routes yielding substantial selectivity utilising bioderived compounds and selective reactions and their outlook for commercialisation. Despite their inherent lack of selectivity, thermochemical routes utilising lignocellulosic biomass to chemicals that yield substantial amounts of p-xylene will also be discussed as well as the utilisation of unconventional alternative biomass sources to directly yield aromatics. A simplified schematic summary of the current bio-based routes to *p*-xylene is displayed in Scheme 2.

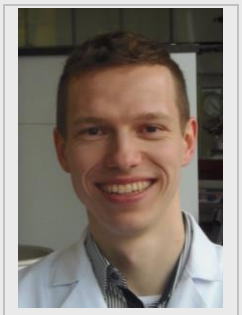


Scheme 2. A summary of several known and speculative routes to biobased p-xylene.

Andy Maneffa received his B.Sc. degree in chemistry from the University of Liverpool in 2015 which included a year as a research chemist at Ineos Technologies (Vinyls) Ltd. He is currently undertaking a M.Sc. in Green Chemistry and Sustainable Industrial Technology at the University of York.



Peter Priecel obtained his Master degree in physical chemistry in 2009 and Ph.D. in heterogeneous catalysis in 2013 at the University of Pardubice with Dr. Libor Čapek and Dr. David Kubička (Unipetrol Research and Education Centre (UniCRE)). Currently he is a Postdoctoral researcher with Dr. Jose A. Lopez-Sanchez and his interests are catalytic biomass conversion and development of metal nanoparticles and porous catalytic materials.



Jose Antonio Lopez-Sanchez graduated in Chemistry in U.R.V (Tarragona, Spain) and obtained his PhD in Cardiff University (UK) in 2003 in Heterogeneous Catalysis with Prof G.J. Hutchings. He is Director of the MicroBioRefinery in the University of Liverpool, dedicated to chemo- and biocatalytic upgrade of biomass utilising high-throughput catalyst discovery with automated robots.

2 Methanol to Aromatics (MTA)

The production of aromatics from methanol has featured patent[12] and open literature[13] since 1970's. Currently, significant interest has been shown to produce renewable methanol and will be shortly discussed towards the end of this chapter.[14] Typically, methanol is converted to the mixture of hydrocarbons and aromatics over acid catalyst (usually MFI type zeolite) at temperatures around 400 °C in a fixed-bed reactor.[13a, 13b, 15] Interest in the methanol-to-aromatics process (MTA) spans from the more intensively studied methanol-to-gasoline process (MTG)[16] as both processes utilise acid catalysts and not too dissimilar reaction conditions producing mixture of hydrocarbons and aromatics. Both MTG and MTA, but especially MTA research has mainly focused on the modified MFI type catalysts.[15] Investigations on modifying the zeolite with oxides of metals such as Cu,[15c] Ni,[15c] Ag,[15b, 15c] Ga[15d] or Zn[15e, 15f, 17] agree that addition of these oxides provides further acid[15e] or basic[15c] sites to the zeolite materials resulting in increased activity and selectivity towards the aromatic products. For example, Inoue et al.[15b] showed that Ag^+ ions promote the dehydrogenation activity of produced alkanes to alkenes, which are believed to be the building blocks of the aromatics.[15c] However, increased aromatisation degree produces more heavy products and therefore deactivation of the catalysts by coking.[15e] Chen and co-workers[18] achieved an increase in both concentration of Lewis acid sites, acid strength and pore size by simply mixing γ-alumina with ZSM-5 which promoted the production of aromatics.

All of the above-mentioned research papers reported high yields of p-xylene among the aromatic fraction, however, several studies concentrated specifically on this target molecule.[15i, 19] Niziolek et al.[19] presented a comprehensive techno-economical study for aromatics refineries which would be feasible and

profitable for production of BTX (benzene-toluene-xylene) aromatic fraction with greenhouse gas emissions comparable or lower than current fossil-fuel-based ones. Natural gas was selected as a source for the production of aromatics, although this could be easily substituted by bio-derived methane or syngas produced from the gasification of almost any lignocellulosic biomass waste. [14a-c] Various commercial and novel technologies were compared, such as MTA, toluene alkylation with methanol, selective toluene disproportionation, toluene disproportionation or transalkylation with heavy aromatics. Generally, more than 75 % yield of aromatics could be achieved and a hypothetical refinery producing aromatics along with gasoline and electricity was found to be viable with ca. 6 year payback periods. Among studied technologies, MTA process was shown to be able to achieve 90 % aromatics yield in the organic fraction.[15i] Zhang and co-workers[15i] have demonstrated that doping of H-ZSM-5 by Zn, P and SiO_2 can increase the selectivity to *p*-xylene in xylenes from ca. 24 to almost 90 % at close to 100 % methanol conversion and 61.7 % total aromatics yield. These calculations give ca. 24 % total *p*-xylene yield, which would however require separation as it is in any existing BTX process. One further consideration to take into account is the rapid deactivation of the zeolite during the MTA process. Although catalytic activity can easily be regenerated via catalyst calcination at high temperatures, deactivation by coke proceeds substantially faster as compared to conditions where the desired products are DME, gasoline or light olefins.

However, the question of sufficient and cheap renewable methanol still arises.

Nowadays, methanol is produced from fossil-fuels-based synthesis gas,[20] however, it would be possible to obtain it from renewable sources and particularly from biomass-derived waste.[14a-c] Currently, there are two routes which are explored the most, namely oxidation of methane[20a, 21] or hydrogenation of CO_2.[20, 22] Use of the latter reduction route is a way of chemically storing hydrogen gas as well as utilisation of carbon dioxide which is currently the most closely followed greenhouse gas.[23] Methane for the oxidation could be recovered either from natural gas resources[20], biomass[24] or even landfills.[14c] In the latter case, biomass-derived methane can come in both pure methane[24] as well as in synthesis gas form.[14c, 20b]

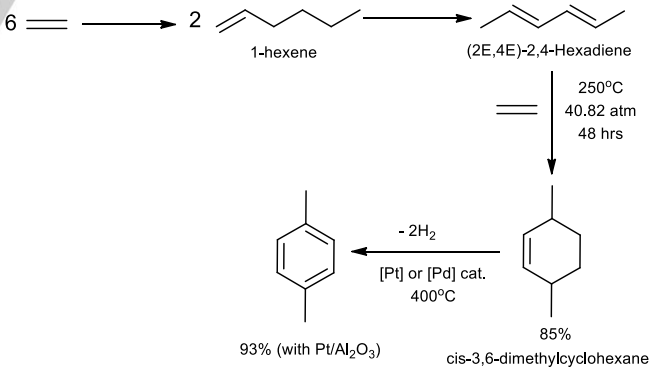
Based on the data and information provided in the literature it seems that this route might be of considerable interest in the future as the transition via natural gas offers chance to further develop biomass-based route. Nevertheless, as biomass gasification technologies have advanced, this pathway to *p*-xylene wouldn't depend on the biomass source as much as the other routes and offers wide product portfolio (e.g. gasoline, other aromatics, olefins).[25] It was suggested that feedstocks for biomethanol synthesis[14a-c] can be produced for example by the gasification of biomass [25] via aforementioned methane[24], CO_2[20a, 26] or synthesis gas route.[20b, 26b] Alternatively, glycerine can be employed to produce renewable methanol as demonstrated by Dutch BioMCN.[14d] Other initiatives and sources to produce biobased methanol include BioMCN bio-synthesis gas[14e], Icelandic Carbon Recycling International from carbon dioxide and hydrogen[14f], Canadian Enerkem from waste-based syngas[14g], U.S. Oberon Fuels from bio-syngas[14h], and other projects aim to generate renewable methanol exist such as German Bio-M[27] or Finnish Uhde.[28]

3 Synthesis of biobased *p*-xylene from C_2 compounds

3.1 Ethanol/ethylene route

Routes to *p*-xylene derived from ethanol/ethylene are, in principle, very attractive due to the existing infrastructure and know-how developed in high volume bioethanol production for liquid fuels. As a consequence, high volumes of biorenewable ethylene can, in principle, be obtained via catalytic dehydration of bioethanol in the locations where bioethanol is produced with very good Life-Cycle Analysis (LCA). Indeed, the production of bioethylene from ethanol for the production of 100 % bioderived polyethylenes has been commercialized successfully by Braskem (Triunfo, Rio Grande do Sul, Brazil) using sugar cane as a raw material for fermentation.[29] This technology is now mature. There is an obvious competition for the utilisation of bioethanol as it is already valuable as fuel, and both cost and LCA will restrict the geography where this technology can be sustainably introduced. The opportunity to upgrade ethanol to ethylene and further to *p*-xylene also offers potential flexibility and expansion of existing operations from bioethanol. More speculative is also the view that future developments in biotechnology might offer alternatives to the need for the current route (sugar cane->ethanol->ethylene) and afford the development of new microorganisms able to produce ethylene directly from waste biomass.[30]

Among the several options available to produce *p*-xylene from a C_2 substrate, Lyons et al.[31] recently reported that *p*-xylene can be produced using ethylene as the only feedstock. The overall synthesis of *p*-xylene from ethylene is depicted in Scheme 3.



Scheme 3. Reported route to p-xylene from ethylene.[31]

The first step of the process consists of the selective trimerisation of ethylene to 1-hexene, an extensively studied and industrially practised reaction which typically employs chromium-based catalysts.[32] Disproportionation of 1-hexene at 180 °C via a transfer dehydrogenation reaction with a second equivalent yielded a mixture of products, which included the target (2E,4E)-

2,4-hexadiene at *ca.* 15 % of the overall product distribution.[31] This step was catalysed with an iridium pincer catalyst (0.04 mol. %, Figure 2) with a turnover frequency of 222 h^{-1} and turnover number of 777.

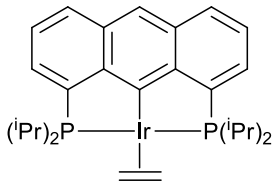


Figure 2. The iridium pincer catalyst employed by Lyons et al.[31]

Next, (2E,4E)-2,4-hexadiene undergoes cycloaddition with ethylene (at 250 °C, 40.82 atm) to give the target *cis*-3,6-dimethylcyclohexane in addition to 3-ethylcyclohexene at a 8:1 ratio and 96 % overall conversion. Finally, *cis*-3,6-dimethylcyclohexane is dehydrogenated to *p*-xylene over platinum or palladium based catalyst at a high yield (93 % observed when Pt/Al_2O_3 at 400 °C was used).

In terms of economic and commercial viability, the first step of the synthetic route already appears to be industrially established as 1-hexene is produced via oligomerisation of ethylene[33] at a high yield, purity and mild conditions (115 °C and ambient pressure) for example by Chevron Phillips Chemicals' Ziegler process, INEOS' modified Ziegler process, Shell's higher olefins process (SHOP), Idemitsu's ethylene oligomerization process, Vista's Alfene® process, Exxon's ethylene oligomerization process, DuPont's Versipol™ process or SABIC/Linde alpha-SABLIN™ process .[33c] This heavily contrasts with both the second and third steps of the synthetic process which require further developments if the route is to be successful. Firstly, the selectivity and overall yield of (2E,4E)-2,4-hexadiene from transfer dehydrogenation could be substantially improved both to increase overall *p*-xylene production and minimise that of unwanted side products. The high temperature and pressure required in the Diels-Alder cycloaddition step is likely to be highly energy intensive, reducing to some extent the green credentials of process. Some of the overall costs of the process could be partially mitigated by the generation of ethylbenzene as a by-product of the final synthetic step (formed via dehydrogenation of 3-ethylcyclohexene) due to its high value as a precursor to styrene.[34]

3.2 Acetic acid route

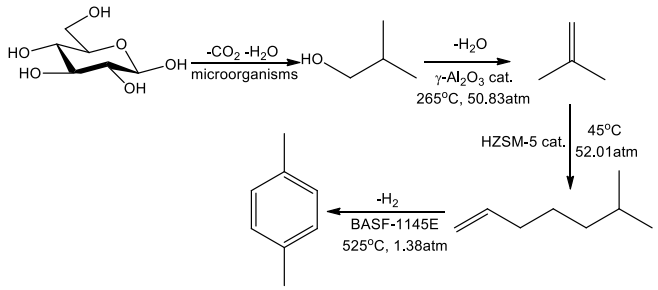
Acetic acid can be obtained from various bio-derived sources,[35] particularly by carbonylation of biomethanol,[36] or fermentation of biomass, for example C_5 and C_6 sugars to ethanol[37] and subsequent oxidation of ethanol to the acid.[38] Ethanol to acetic acid can be performed e.g. by heterogeneously catalysed selective oxidation of ethanol[38] or oxidative fermentation with *Acetobacter*.[39] Alternatively and more speculatively, acetic acid could be obtained from the aqueous fraction in the low temperature microwave pyrolysis of lignocellulosic biomass, although it would need to be separated from within a product mixture of the process.[40]

A recent joint patent by Archer Daniels Midland Company and Washington State University[39] describes the production of *p*-xylene from acetic acid. In the first step, acetic acid is converted into isobutene in an aqueous phase flow reactor over a $Zn_xZr_yO_z$ mixed oxide catalyst at 415 °C in 50 % yield. Isobutene is then dimerised into isooctenes over commercial ZSM-5 catalysts at 175 °C and 50 bar in 60 % yield. Isooctenes are finally dehydrocyclised into xylenes over commercial chromium oxide doped alumina catalyst at 550 °C and atmospheric pressure in 60 % yield. It was claimed that 99 % of the xylenes is *p*-xylene. However, the total yield of *p*-xylene in this process is only *ca.* 18 % opening the question whether this is a sufficient yield to make the process profitable, but at the same time opening a door to developing new improvements.

It is important that Life Cycle Analysis are rigorously performed particularly regarding these C_2 based routes due to their almost complete reliance on bio-derived ethylene/ethanol production which are currently produced from food crops. Looking towards the future, inevitable increase in global population and growth of emerging economies is certain to put considerable burden on food sources and land use, thus, the availability of the traditional natural feedstocks for bioethanol may plummet having serious implications on the overall viability of *p*-xylene solely from ethylene. Although the same rigorous analysis must be performed in other routes to bio-derived *p*-xylene, we must emphasise the need to developing efficient routes to cellulosic ethanol. Also, further technological improvements are required to lower the cost of bio-ethylene, which is currently between 1.1-2.3 times higher than the global average price of petroleum derived ethylene[41] and has the greatest single influence on the economic viability of this particular route to biomass-derived *p*-xylene. On the other hand, bio-derived ethylene is currently commercially produced by simple dehydration of ethanol by Brazilian Braskem[29] and improvements in the development of more efficient catalytic systems with better diffusion and deactivation profiles can potentially lead to reductions in the price of bioethylene. Also, thanks to the various emerging technologies available for fermentation of more sustainable types of biomass, it is plausible to expect that more sustainable and sufficient production of bio-based ethanol will be attained in the near future without competing with food crops.[37a, 37b, 37d-g]

4 Converting isobutanol to *p*-xylene

Isobutanol has received a lot of attention as an important bioderived chemical owing to the fact that it can be produced from biomass at high yields, can be used as an energy-dense, high-octane biofuel and also as a precursor to important commodity chemicals.[42] In 2011, Gevo, Inc., a company specialising in the production and subsequent conversion of biobased isobutanol, patented a process for the production of *p*-xylene from isobutanol.[43] A schematic overview of this process is depicted in Scheme 4.



Scheme 4. Gevo Inc. process for converting isobutanol (from glucose) to p-xylene. BASF-1145E is commercial chromium oxide catalyst.[44]

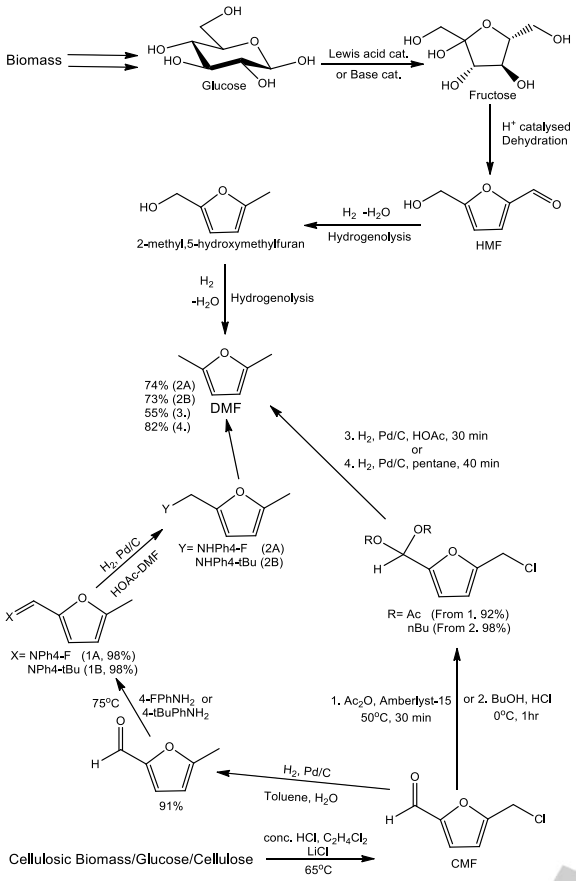
Lin et al.[44] provide a summary of the route where isobutanol is first obtained via conversion from glucose (derived from the saccharification of starch) using metabolically engineered microorganisms. Isobutanol then undergoes subsequent dehydration (at 265 °C and 50.83 atm) to isobutene over γ-Al_2O_3. H-ZSM-5 catalysed oligomerisation of the obtained isobutene (45 °C, 52.01 atm) affords *iso*-octene which is finally dehydrocyclised at 525 °C and 1.38 atm to give *p*-xylene using a commercial chromium oxide catalyst (BASF-1145E).[45] Dodds and Humphreys reported that the complete process yields 18.7 kg *p*-xylene per 100 kg glucose.[46]

The fact that the Gevo's route from isobutanol has already been commercialised within the biorefinery in Silsbee, Texas, U.S.A. in collaboration with South Hampton Resources Inc.[47] suggests that it is at least partially, economically viable, despite the fact that several of the steps involved, operate at noticeably high temperatures and pressures (>50 atm) and are energy intensive. Even if the costs of these steps are not too detrimental to the overall economics of the route, the green credentials could be somewhat tainted as most energy would still be ultimately derived from petroleum based sources. In light of this, any improvements to the process whereby yields can be maintained or improved whilst reaction conditions approach ambient ones would make this route to biomass-derived *p*-xylene even more attractive. In this specific case it was shown that Gevo, Inc. uses the biorefinery to produce renewable jet fuel and octane along with aromatics. This diversity might be the reason for the feasibility of the integrated concept. Lin et al.[44] also noted that in the Gevo process,[43] many of these by-products (*e.g.* xylene isomers) are difficult to separate, again requiring more energy and costs although solid waste obtained from the fermentation step could possibly be burnt as fuel or sold as animal feed. The same authors calculated that with consideration of by-product value, the minimum price (i.e. where net present value is equal to 0) of *p*-xylene produced via this route is \$3481 t^{-1}. This value is considerably higher than that of petroleum derived *p*-xylene (\$1630 t^{-1})[44] and so, must realistically be reduced by a considerable margin before this route becomes a serious alternative to more traditional routes. The dependence on isobutanol as a feedstock might also be seen as a weakness. However, Gevo Inc. successfully runs a fermentation plant for isobutanol in Luverne, MN, U.S.A.[47] and recently announced partnerships in India, Argentina, Canada or U.S.A. for more isobutanol plants.[48]

5 Cycloaddition of biomass-derived furans and suitable dienophiles

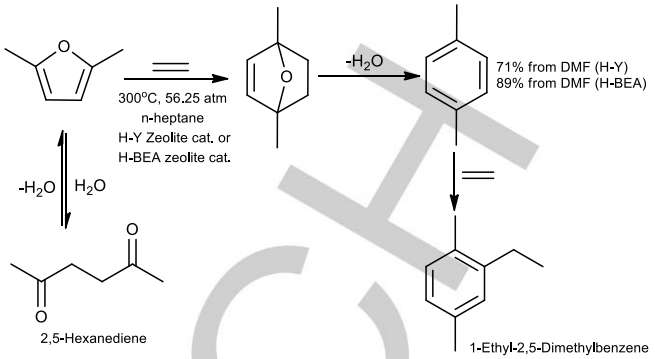
One of the best studied routes to biobased *aromatics* is based on the controlled Diels-Alder cycloaddition of furanic compounds with suitable dienophile molecules, where both substrates can be derived from biomass. To produce *p*-xylene, 2,5-dimethylfuran (DMF) is used as the diene component of the reaction and ethylene as the dienophile. DMF production from biomass has been well documented (Scheme 5).[49] Typically, glucose can first be isomerised to fructose by either heterogeneous Lewis acid[50] or basic catalyst[51] before being subsequently converted to HMF via acid-catalysed dehydration.[52] Once obtained, HMF undergoes hydrogenation to give DMF (via 2-methyl-5-hydroxymethylfuran) as demonstrated by different research groups.[53] Recently, Dutta and Mascal have reported a route to DMF from raw biomass under mild conditions including subsequent reduction of intermediate 5-(chloromethyl)furfural (CMF).[54]

In the production of *p*-xylene, DMF is reacted with ethylene in a Diels-Alder cycloaddition reaction yielding an oxabicyclic cycloadduct which undergoes dehydration to give *p*-xylene.[49c] This dehydration step has been catalysed by different Lewis and Brønsted acids such as zeolites[55] and other aluminosilicates and metal oxides.[56] Despite catalytic enhancement of the reaction, the [4+2] cycloaddition of DMF with ethylene still requires substantial energy input due to the large HOMO-LUMO gap that exists between the reacting species.[57] Because of this, such reactions typically require relatively high temperatures (200-300 °C) and pressures (>50 bar) to achieve satisfactory results. [55a]



Scheme 5. Several reported pathways to biobased DMF.[53b, 54]

Recently, Williams and co-workers[55a] aimed to explore the mechanism and route to selectivity involved in *p*-xylene production from DMF and ethylene while using several heterogeneous catalytic systems. It was revealed that the initial Diels-Alder cycloaddition is the rate limiting step and can be promoted via confinement within the zeolite micropores. In addition, the subsequent dehydration of the oxabicyclic type intermediate can be effectively catalysed by Brønsted acid sites containing catalysts. The group also demonstrated that a H-Y zeolite (Si/Al = 2.6) could be used to give *ca.* 75 % selectivity along with high conversion (*ca.* 95 %) of DMF at 300 °C and 56.25 atm using *n*-heptane as the solvent (Scheme 6).



Scheme 6. Production of p-xylene from cycloaddition of DMF and ethylene with competing reactions.[55a]

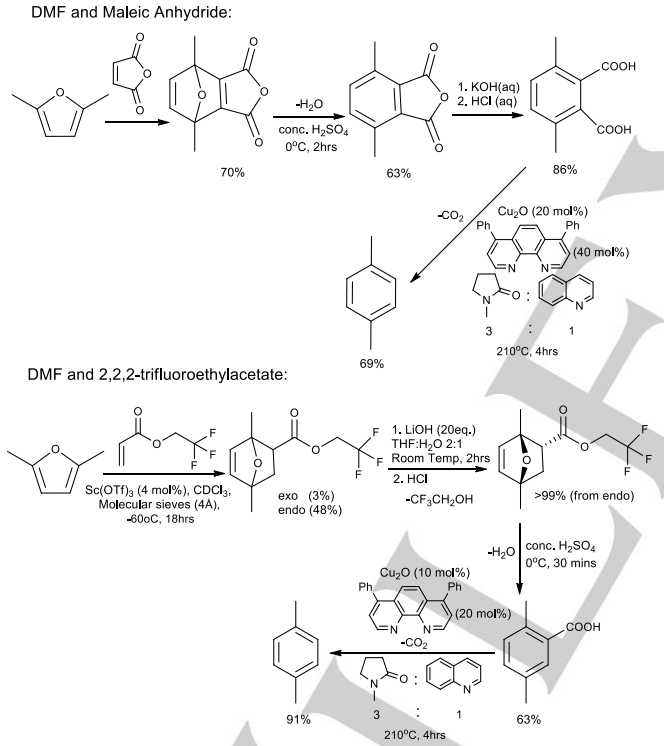
The solvent aliphaticity and reaction temperature were shown to be important in minimising competitive side reactions (e.g. hydrolysis of DMF and alkylation of *p*-xylene to 1-ethyl-2,5-dimethylbenzene). In a later study it was shown that the improved results observed with *n*-heptane were a result of increased ethylene and decreased water adsorption in the zeolite pores. This effect was explained to be due to the enhanced hydrophobicity of the reaction environment.[58] On the other hand, Wijaya and co-workers[56] found that polar aprotic solvents such as 1,4-dioxane or THF offer improved dehydration reaction rates compared to heptane. Authors suggested that the polar solvent better stabilizes the charged intermediate during the dehydration step and supported their hypothesis by two other studies focusing on the dehydration of biomass-derived compounds.[59]

In a DFT study, Nikbin et al.[57] concluded that Brønsted acid catalysis is necessary to promote the oxacyclic intermediate dehydration at a reasonable rate. It was also shown that even though the cycloaddition step can proceed uncatalysed, Lewis acids were effective at catalysing this step.[60] Therefore, a bifunctional catalyst (containing both Lewis and Brønsted acid sites) may be optimal. In a subsequent paper, Chang and co-workers[55b] reported that a H-BEA zeolite catalyst can be used to give *p*-xylene at a 90 % yield (>90 % product selectivity and 99 % conversion of DMF). The superior performance of H-BEA was attributed to its resistance to deactivation, greater activity and preferential dehydration of the cycloadduct intermediate to *p*-xylene as opposed to undesirable side products. It was also shown recently that silica-alumina aerogels with high mesopore area and acidity can achieve comparable catalytic activities as H-BEA.[56]

Although ethylene is the main dienophile used with DMF to produce *p*-xylene, alternatives have been suggested. For example, Shiramizu and Toste[61] demonstrated that *p*-xylene could be produced via Diels-Alder cycloaddition of DMF with several novel biomass-derived dienophiles such as acrolein. Maleic anhydride and 2,2,2-trifluoroethylacetate were also shown to give *p*-xylene (Scheme 7).[61] To this end, Mahmoud et al.[62] showed that the substituted phthalic anhydride-like oxanorbornene intermediate (Scheme 7) could also be produced in high yield (96 %) at room temperature in solvent-free conditions with subsequent dehydration to the substituted phthalic anhydride

with 80 % selectivity. Recently, Thiyagarajan et al.[63] demonstrated that hydrogenation of the phthalic anhydride oxanorbornene intermediate can stabilise it and prevents retro Diels-Alder reaction that decreases the yield of the dehydrated product.

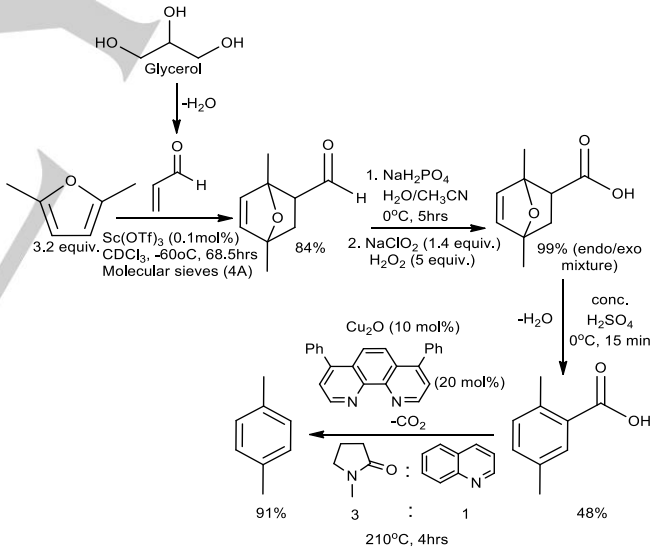
The initial Diels-Alder cycloaddition step of DMF and acrolein has been studied first by Laszlo et al.[64] who had achieved *ca.* 40 % yields of the further unspecified cycloadducts at -43 °C over Fe(III) supported bentonite in a single step in 5 hours. In a more recent study, Shiramizu and Toste reported that the target diastereomeric adducts could be synthesised at 84 % yield (-60 °C, 68.5 h) using $Sc(OTf)_3$ as a catalyst in addition to activated molecular sieves (4 Å). The low reaction temperature was found to be crucial in minimising acrolein decomposition which was heavily detrimental to the reaction. Moreover, the molecular sieves acted to prevent deactivation of the Sc catalyst by water, which was necessary for maintaining a reasonable reaction rate. Once the target adducts had been obtained, the catalyst was subsequently quenched at -55 °C via addition of an aqueous NaH_2PO_4/CH_3CN mixture.



Scheme 7. Reported routes to p-xylene from DMF and maleic anhydride/2,2,2-trifluroethylacetate.[61]

Following this, the reaction mixture was allowed to warm to 0 °C before H_2O_2 and $NaClO_2$ were added resulting in the oxidation of diastereomeric adducts to the corresponding carboxylic acids. It was concluded that oxidation was necessary to prevent retro-Diels-Alder reactions that were observed if the adducts were heated above -60 °C. The acid species were subsequently treated with concentrated H_2SO_4 to yield 2,5-dimethylbenzoic acid (48 % yield) which underwent Cu_2O-catalysed protodecarboxylation at 210 °C to give *p*-xylene (91 % yield). Overall, this synthetic route led to successful *p*-xylene production from DMF and acrolein at a 34 % yield (summarised in Scheme 8).

In their recent 'Life cycle assessment of biobased *p*-xylene production', Lin et al.[65] concluded that production of *p*-xylene starting from starch and proceeding via Diels-Alder cycloaddition of DMF and ethylene was actually still less 'environmentally friendly' than that derived from petroleum, highlighting the need to further improvements in the efficiency and sustainability of the process. The same group also calculated that the minimum price to biobased *p*-xylene (when by-product value is considered) following the aforementioned cycloaddition route was \$2885 t^{-1} and significantly more expensive than its petroleum based counterpart (\$1630 t^{-1}).[44] It was noted that the most significant cost of the process is the high price of vital raw materials, namely HMF, which represents an inherent problem for the economic feasibility of such routes. There is an enormous ongoing effort from academia and industry to improve HMF production. When cheaper and more sustainable production methods for these important biobased reactant will be implemented, this will have an immense impact in lowering the overall cost to renewable *p*-xylene; whereas also improved catalytic systems working with greener solvents and milder conditions are required for the outcome of the life cycle assessment to be further improved.



Scheme 8. Synthesis of p-xylene from DMF and acrolein.[61]

The Diels-Alder cycloaddition of ethylene and DMF requires considerable energy input to overcome the significant HOMO-LUMO gap that exists between the two substrates. Typically, high reaction pressures and temperatures are needed, and these processes are energy intensive resulting in an economic and environmental cost. In a similar way when using acrolein as the dienophile, all four of the mechanistic steps require either significant cooling or heating in order to achieve acceptable results. Maintenance of such reaction temperatures is also energy

intensive and to improve both the economic viability and overall green credentials of both routes, reaction conditions should ideally become more ambient. Unfortunately, the inherent nature of the initial Diels-Alder steps involved in these pathways means that this would be difficult to achieve. For instance, the cycloaddition of DMF and acrolein is thermodynamically controlled, making lower reaction temperatures a fundamental requirement regardless of what catalytic system is used.[61] There is the scope to improve the viability of both routes however, for example, through modifications in the catalyst, such as producing mesoporosity using hierarchical zeolites[66] and solvent systems of ethylene addition to DMF as discussed previously. Similarly, the acrolein route utilises a dehydration product of glycerol which, in turn, is a widely available and cheap by-product of biodiesel production.[67] Ultimately, both routes would require further optimisations in order to move towards future commercialisation although it appears that the one which utilises ethylene is somewhat closer.

6 Routes for direct conversion of lignocellulosic biomass to aromatics

Up to know we have highlighted routes to *p*-xylene utilising bioderived compounds from biomass that can be selectively produced. In this section however, we will highlight another approach whereby routes are inherently less selective by utilising thermochemical methods to transform lignocellulosic biomass to a wide range of bioderived products from which *p*-xylene can be isolated within a myriad of other aromatic compounds.

6.1 Catalytic fast pyrolysis

It has recently been reported that catalytic fast pyrolysis (CFP) could become an effective method of direct aromatics production from biomass, including that of *p*-xylene.[68] In general, fast pyrolysis describes a high temperature process where a feedstock is rapidly heated (>500 °C) in the absence of oxygen at very short residence times to generate vapours which are then rapidly cooled to produce pyrolysis/bio oil.[69] After being generated, the pyrolysis vapours are converted to the target compounds when passed over catalysts, typically zeolites. CFP has some attractive features in that it is relatively simple (all desired reactions occur within one single-step reactor) and inexpensive (employing a widely available aluminosilicate catalysts) although the process is energy intensive and also produces several undesirable by-products such as carbon oxides and coke.[70]

The conversion of lignocellulose to aromatics via CFP follows a general pathway; (1) formation of anhydrous sugars from the hemi/cellulose components of the biomass, (2) dehydration of these sugars to furanics, (3) acid catalysed oligomerisation, decarbonylation, decarboxylation and dehydration of the furanics (over the zeolite) to aromatic products. In addition to untreated biomass, it is also possible to produce 6-membered aromatics by directly subjecting furanic compounds such as HMF[71] and furfural[72] to CFP.

The relative amounts of the final products are inherently dependent on the original biomass source although methods to improve the selectivity of the process are being explored. For instance, Cheng et al.[68] demonstrated that selective synthesis of *p*-xylene from CFP of 2-methylfuran in helium/2 % propylene increased *p*-xylene selectivity from 5 to 15 % when the pore size of the zeolite was reduced using silicon alkoxides. A similar result was also noticed when gallium was used in the place of the silicon alkoxides, however, both modifications appeared to have a negative effect on the overall catalytic activity. The authors concluded that the narrowing of the pore openings of the catalyst caused more space confinement leading to greater para selectivity (represented qualitatively in Figure 3).[68]

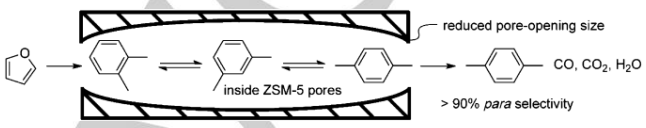


Figure 3. A representation showing the diffusion limitations of xylene isomers inside the pores of a zeolite. Reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Copyright 2012.[68]

The conversion of lignocellulosic biomass to aromatics, including *p*-xylene using CFP is in the process of being commercialised by Anellotech, Inc.[73] They claim to be able to use a variety of different biomass sources (wood waste, corn stover, sugar cane bagasse, etc.) as a feedstock. In general, the route to *p*-xylene using CFP of biomass has attractive features, for instance the simplicity, availability and low cost of the primary feedstock and zeolite catalysts. Also, as it has been shown to work for waste and lignocellulosic sources of biomass, the route is not likely to be food-competitive. However, high reaction temperatures are used requiring considerable energy input. Also, a large amount of unwanted by-products is generated, but these are mostly aromatic compounds which could be processed in the bio-refinery. Without the aid of a LCA or techno-economic analysis, we suggest that the above, together with the generally low overall *p*-xylene yield somewhat detract from the green credentials and economic viability of the overall process and must certainly require optimisation to improve the future outlook of the route.

6.2 Lignin depolymerisation/hydrotreating route

Other more direct route of producing aromatic, i.e. benzene-toluene-xylene (BTX) fraction and in particular *p*-xylene, is the depolymerisation of lignin via deoxygenation and hydrotreating processes. Literature provides several extensive reviews on comparison of these pathways for lignin processing.[11c, 11d] In most cases the liquid yield from lignin processing varies greatly and is rarely close to <80 % and usually <50 %.[11c] On top of that, not all of the liquid fractions are aromatic compounds. Joffres et al.[74] obtained 9 % yield of aromatic monomers via hydrotreating using sulfided NiMo catalysts from which BTX and *p*-xylene could be extracted. It should be noted that this not so encouraging result

was achieved using temperatures around 350 °C and H_2 pressures up to 80 bar.

Despite this, multiple reports[75] describe real possibility and development of processes for production of BTX from biomass and specifically lignin. Companies such as Biorizon[75b] and Lux Research[75e] predicted industrial application and processing of lignin into BTX to emerge around 2019-2021. These predictions are based on known historical relationship of research, patents and commercial development. Recent patents on direct conversion of lignin into aromatics by companies such as UOP LLC[76], Procter & Gamble[77], Aligna Technologies, Inc.[78] or Biochemtex S.P.A.[79] suggest that such technologies might have a commercial future. More companies such as Annikki GmbH[80] or Biome Bioplastics[81] are investigating selective lignin degradation for plastics or platform chemicals production.

Despite the complexity of the feedstock, the harsh reaction conditions, complexity of the product mixture and the very low potential yields towards *p*-xylene, one needs to acknowledge that the processes involved are no different to many currently undergoing in the petrochemical industry, so that the lack of selective chemistry might not be a serious problem for eventual commercialization.

6.3 Commercial deoxygenation-condensation pathway

Apart from lignin only, various biomass sources were reported to be suitable for the following commercialised two-step process to produce *p*-xylene. Virent, Inc. and Coca-Cola Company teamed up[82] to use Virent's BioForming® process and started production of BioFormPX® *p*-xylene.[83] *p*-Xylene in this two-step process[84] is produced from biomass derived and water-soluble oxygenated hydrocarbons (e.g. starch, cellulose, lignin derivatives), which are deoxygenated in the first step over transition and noble metal supported catalyst typically containing metal oxide as a support at 200-280 °C and H_2 pressure up to 90 bar. The second step is the acid catalysed vapour phase condensation of the deoxygenated mixture, typically over Cu, Ni, Ga, Zn supported ZSM-5 at 125-450 °C and up to 50 bar, producing a mixture comprised of ca. 64 vol. % of aromatics. *p*-Xylene can then be extracted from this mixture via well-known and established refining technologies.

7 Perspective on *p*-xylene production from novel biomass sources

In addition to some of the previously mentioned and more familiar biomass-derived routes that have been discussed, there is the potential to produce *p*-xylene from naturally occurring compounds which already contain the target within their native structures. Production of cyclic aromatics from lignin is currently receiving and has already received considerable interest[85] and so, cannot be classed as completely a 'novel' idea.

Biotechnology might be a future emerging technology for bioderived aromatics as Liu et al.[86] reported the production of two prenylated *p*-xylenes by Caulerpa racemosa, an abundant species of green algae found in shallow marine environments. The discovery of these two molecules, caulerprenylol A (Figure 4a) and B (Figure 4b) is significant because scarcely any naturally occurring prenylated *p*-xylenes have been isolated and reported. The *α*/*β* members of the two related families of compounds that constitute vitamin E; tocotrienols (Figure 4c) and tocopherols (Figure 4d),[87] make up most of the few such examples, along with occidol (Figure 4e)[88] and rishitinol (Figure 4f)[89] which can be found in Thuja occidentalis and various species of Solanum, respectively.

A critical aspect which would affect the viability of *p*-xylene production from each of these natural sources is the difficulty and practicality of synthesis. Due to their highly functional structures, any synthetic processes leading to *p*-xylene are likely to be multi-step and complex making them expensive. A few transformations that may be potentially applicable to the aforementioned molecules are known, for instance the hydrogenolysis of phenol to benzene.[90]

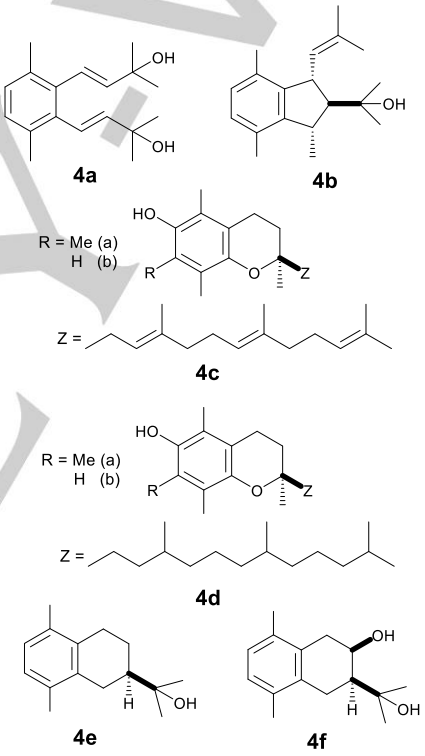


Figure 4. The structural formulae of: Caulerprenylols A (a) and B (b), α and β tocotrienols (c), α and β tocopherols (d), occidol (e) and rishitinol (f).

However, most of the necessary transformations will involve removal of multiple, predominantly carbon based functional groups which is uncommon and would require very selective C-C bond cleavage of these target phenyls. There are very few reactions of this type that have been reported historically and research within this particular field still remains at a fledgling stage.[91] Apart from the fundamental problems faced in such reactions (e.g. the steric inaccessibility of C-C bonds[92]), one of main challenges from a design standpoint is the difficulty of finding

a sufficiently selective catalyst or enzyme which, in turn is inherently required due to hyper selective nature of the desired transformations. Again, such development would be costly and only realistically achievable in the long term.

Another aspect that needs to be considered is the level and efficiency of production of the target molecules from each of their corresponding natural sources. Due to the naturally low amounts of the compounds in their respective sources, large quantities of each source would be required. For example, a study conducted by Andersen et al.[93] suggested that the amount of occidol present in fresh and dried Thuja occidentalis hardwood was 0.21-0.35 % and 0.32-0.46 % mass, respectively. Similarly, Swern [94] reported that α and *β* tocopherol content of wheat germ oil was only 0.12 % and 0.04 % mass respectively. Taking the highest value for occidol and combining the values for *α* and *β* tocopherol (as they would both be converted to *p*-xylene), the theoretical amount (assuming 100 % yield in all steps) of Thuja occidentalis and wheat germ oil required to produce 1 kg of *p*-xylene would be 447 kg and 2514 kg, respectively. Both of the calculated amounts are considerable and too high for production from these sources to be viable, even if the chemistry of the synthetic processing steps was developed and optimised. Viability could be improved for instance, if the >99 % of the natural sources not used could be effectively utilised, for example, by transformation into other chemicals or directly as fuel.

The production of the target natural compounds could be improved via metabolic engineering as exemplified in work conducted by Shintani and DellaPenna[95] who demonstrated that it was possible to increase levels of *α* tocopherol in *Arabidopsis* seeds 80-fold. Such a method could be used to produce the targeted molecules (such as *α* tocopherol) more efficiently, in turn, making the overall process more economical.[96] However, research within this area is not particularly established and requires considerably more work to build upon promising initial studies.

A final factor that must be considered is the potential impact on other important resources that would come with large scale cultivation of the target natural sources for *p*-xylene production. For instance, use of wheat and Solanum would directly compete with food production, potentially having catastrophic impacts on areas where these crops are heavily relied on for food and nutrition. In this aspect, the utilisation of, caulerprenylol A and B has an advantage in that they are derived from marine based organisms minimising the indirect competition with arable land that the other sources would entail.

8 Conclusions and outlook

The need to source commodity chemicals, of which *p*-xylene is a very important example, in a renewable manner is a challenge that must be addressed in order to ease the burden on the production from ever diminishing non-renewable sources. The potential implementation of such routes would have tremendous impact on the production of more sustainable polyester fibres and PET bottles in particular, with important environmental consequences. Regarding the routes to *p*-xylene starting from bioderived compounds and their potential commercialisation, we highlight that Diels-Alder cycloaddition of DMF and bio-ethylene and the synthesis from isobutanol appear more advanced and attractive in the short/medium term. In both routes, the chemistry has been well established but there are still some tantalising challenges to be addressed. For instance, the cycloaddition of DMF and ethylene typically requires high temperatures and pressures and the maximum theoretical yield of *p*-xylene from isobutanol is below 40 %. In addition to these factors, the costs of both routes are largely dictated by the price of certain feedstocks (namely DMF and isobutanol, respectively) which increases their economic unpredictability. Ultimately, cheaper and greener production of HMF is also required. The reliance on a single feedstock is most pronounced when considering *p*-xylene synthesis exclusively from bio-ethylene, but on the other side, the availability of oil-derived ethylene helps to reducing risk and affords flexibility in the process. Despite energy requirements and other process limitations, the existing commercial production of bioethylene and biopropylene derived from sugar cane by Braskem in Brazil is clear proof that this route has a great potential.

On the other hand, the production of aromatics via CFP has many attractive features, for instance, the abundance of raw materials and the relative simplicity of using pyrolytic processes. However, the cost of separation process is a drawback and overall yields of *p*-xylene must be increased to improve future prospects for this particular aromatic compound. One way to alleviate this situation could be the Virent approach, which should be applicable to different biomass sources and has been demonstrated to work on a commercially relevant scale.

A route that shouldn't be ignored is the methanol route as it could use almost any form of biomass that after gasification could be transformed either into methanol and consecutively aromatics and other products or directly via Fischer-Tropsch to the mixture of organic compounds. This route alone could make for a bio-refinery on its own and could employ many of the already established refining processes. The opportunity of utilising bioethanol in the same dehydration processes would add further flexibility to the biorefinery.

Finally, several novel biomass sources for potential *p*-xylene production were introduced. The highlighted compounds allow consideration of what may be possible in long term, but commercialisation from these substrates in the near future is very unlikely.

To summarise, following technological advancements over the last five to ten years, production of biomass-derived *p*-xylene is becoming closer to succeed in the short term. Despite this, most of the routes mentioned are still dependent on abundant, sustainable and cheap feedstocks and the catalytic technologies still require further optimisation, particularly in terms of selectivity and operating conditions, in order to improve their individual prospects for commercialisation. We foresee an intensification of efforts in recent years, both from industry and academia to overcome technological limitations and produce superior catalytic systems that will enable the realisation of commercial, cheap and sustainable production of bioderived aromatics within the emerging bioeconomy.

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Keywords: renewable aromatics • biomass to aromatics• zeolites • catalysis • *p*-xylene

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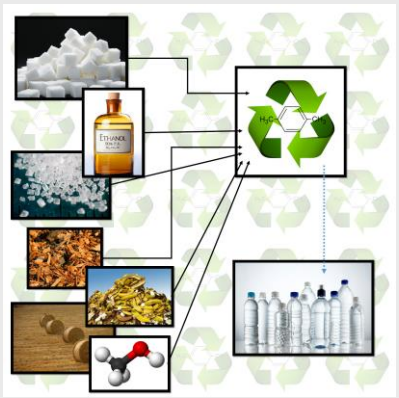

*Andy Maneffa, Peter Priecel, Jose Antonio Lopez-Sanchez**

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